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RHEOLOGY OF CONCENTRATED SUSPENSIONS
OF SPHERES. III. SUSPENSIONS AGGLOMERATED
BY AN IMMISCIBLE SECOND LIQUID

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A theory was developed in an attempt to explain the experimental results. The theory predicts pseudoplastic flow behavior for agglomerated suspensions, but the quantitative correlation between theory and experiment is not satisfactory.

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BY

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FOREWORD

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Rheology of Concentrated Suspension of Spheres

III. <u>Suspension Agglomerated by an Immiscible Second Liquid</u>

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Abstract

Small amounts of a second immiscible liquid, water, were introduced
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bridges between the particles and caused the suspensions containing
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flow behavior from Newtonian to pseudoplastic. The extrapolated
Bingham yield stress went through a maximum as the amount of water
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A theory was developed in an attempt to explain the experimental
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Rheology of Concentrated Suspensions of Spheres

III.   Suspensions Agglomerated by an Immiscible Second Liquid

Introduction

The effect of liquid bridges between particles on the rheological behavior of granular materials has been a subject of investigation for a long time (1-6). Most such studies measured the tensile strength of wet granular agglomerates and correlated the strength with the attractive force of the liquid bridges which held the particles together. Liquid bridges also are capable of forming agglomerates in a suspension when the bridging liquid is immiscible with the main suspending liquid (7). However, very little work has been done on the effect of adding a second immiscible liquid to a suspension. The present work studies the role of liquid bridges in suspensions in more detail than past work and tries to correlate the rheological behavior of agglomerated suspensions with the attractive force of the liquid bridge as measured by the interfacial tension between the two immiscible liquids.

Theoretical

The energy balance approach may be used to derive a rheological equation of state for agglomerated suspensions; i.e., the total rate of energy input per unit volume, E_T, is assumed to be the sum of the rate of energy dissipated in breaking agglomerates apart per unit volume, E_B, and the rate of viscous energy dissipation per unit volume, E_V:

$$E_T = E_B + E_V . \qquad [1]$$

It is assumed for mathematical simplicity that the agglomerates maintain an equilibrium size which is a function of the shear rate. At lower shear rates, the agglomerates have a larger diameter than they have at higher shear rates.   In the steady

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state condition at a given shear rate $\dot{\gamma}$, it is assumed that the collision frequency of agglomerates is given by the von Smoluchowski equation

$$\frac{dn}{dt} = \frac{2}{3} n^2 (2R)^3 \dot{\gamma} \qquad [2]$$

where n is the number of agglomerates, and R is the radius of the agglomerates. By equating the tensile force acting on the surface of agglomerates with the cohesive force (liquid bridge force) which holds the particles together, it can be shown (8) that the equilibrium radius R of agglomerates is inversely proportional to the square root of the shear rate:

$$R = \left(\frac{r^2 \dot{\gamma}_c}{\dot{\gamma}} \right)^{1/2} \quad \text{for} \quad \dot{\gamma} < \dot{\gamma}_c \qquad [3]$$

where r is the radius of the primary particles (glass beads), and $\dot{\gamma}_c$ is the critical shear rate above which no agglomerates exist.

In the low shear rate region ($\dot{\gamma} < \dot{\gamma}_c$), the flow units are agglomerates. They will collide to form larger agglomerates which immediately are broken up to form smaller agglomerates that are stable under the particular shear rate. The calculation of that part of the energy which is due to the breaking up of collision pairs of agglomerates follows very closely the method suggested by Michaels and Bolger (9). The equation of Smith, et. al. (10) for relating the coordination number of particles in agglomerates to their porosity is incorporated into the calculation. The rate of energy dissipated per unit volume is then

$$E_B = \frac{6W_o \phi^2 \dot{\gamma}^{3/2}}{\pi^2 r^3 \dot{\gamma}_c^{1/2} \phi^* (1-\phi^*)} \qquad [4]$$

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where W_o is the work needed to break a liquid bridge, ϕ is the volume
fraction of solid particles in the suspension, and ϕ^* is the
volume fraction of particles in the agglomerates.

If the effect of gravity is neglected, the attractive force
caused by the liquid bridge is due to the interfacial tension and
pressure difference between the two liquids. According to Fisher (2),
the attractive force when the two spheres make contact, F_{max}, is given by:

$$F_{max} = 2\pi r\sigma\sin\psi\sin(\psi+\theta)+\Delta P\pi r^2\sin^2\psi \qquad [5]$$

where σ is the interfacial tension, and the angles ψ and θ are shown
in Figure 1. Fisher has calculated this force for various amounts of
liquid between the spheres. From these data, an approximate relation
between the maximum attractive force and the volume, V, of bridging
liquid is

$$F_{max} \doteq 1.56\pi r\sigma \left(\frac{v}{r^3}\right)^{-0.0237} . \qquad [6]$$

Assuming that the volume of every bridge is the same, the volume is
related to the total weight W_B of bridging liquid by:

$$V = \frac{0.860\pi\rho_s r^3(1-\phi^*)}{\rho_B} \left(\frac{W_B}{W_S}\right). \qquad [7]$$

W_B and W_S are the weight of bridging liquid and weight of solid
particles, respectively, in the suspension. The corresponding densities
are ρ_B and ρ_S.

The attractive force caused by a liquid bridge between equal radius spheres shows an approximate linear decrease with the distance between the spheres (11, 12), i.e.,

$$F_X = F_{max} \left(1 - \frac{X}{X_r}\right)$$ [8]

where X_r is the distance between two spheres when the bridge breaks. Experimentally, this rupture distance has been found to be (11)

$$\frac{X_r}{r} = 1.07 \left(\frac{v}{r^3}\right)^{0.348} .$$ [9]

The work W_o required to break one liquid bridge is then

$$W_o = \int_0^{X_r} F_X dX = 0.835 \pi \sigma r \ v^{0.324} .$$ [10]

Therefore, the rate of energy dissipation per unit volume caused by separating agglomerate pairs is

$$E_B = \frac{5.01 \sigma \ v^{0.324} \ \phi^2 \ \dot{\gamma}^{3/2}}{\pi r^2 \gamma_c^{1/2} \ \phi^*(1-\phi^*)} \quad \text{for} \quad \dot{\gamma} < \dot{\gamma}_c$$ [11]

The rate of viscous dissipation per unit volume in a suspension is

$$E_V = \eta \dot{\gamma}^2 = \eta_r \eta_o \dot{\gamma}^2$$ [12]

where η_r is the relative viscosity of a suspension in which no agglomerates are present, and η_o is the viscosity of the pure liquid

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medium. The relative viscosity can be calculated from some well established equations, the Thomas equation (13), for instance. Then

$$E_T = \frac{5.01\sigma\,V^{0.324}\,\phi^2\dot{\gamma}^{3/2}}{\pi r^2\dot{\gamma}_c^{1/2}\,\phi^*(1-\phi^*)} + \eta_r\eta_o\,\dot{\gamma}^2 \quad . \qquad [13]$$

Now, if we assume that the total rate of energy dissipation in the suspension is given by the product of the overall shear rate and shear stress, we obtain for the shear stress τ in the agglomerated suspension:

$$\tau = \frac{5.01\sigma\,V^{0.324}\,\phi^2}{\pi r^2\,\dot{\gamma}_c^{1/2}\,\phi^*(1-\phi^*)}\,\dot{\gamma}^{1/2} + \eta_r\eta_o\,\dot{\gamma} \qquad [14]$$

for low shear rates ($\dot{\gamma} < \dot{\gamma}_c$). This equation suggests that the flow behavior is pseudoplastic.

At high rates of shear ($\dot{\gamma} > \dot{\gamma}_c$) where the flow units are single particles, it can be shown that (9)

$$\tau = \frac{2.51\sigma\,V^{0.324}\,\phi^2}{\pi r^2} + \eta_r\eta_o\,\dot{\gamma} \quad . \qquad [15]$$

This equation suggests a Bingham plastic type of behavior at high shear rates with a yield stress τ_y given by the first term on the right side of the equation.

Materials and Methods

Glass beads of two sizes were obtained from the Cataphote Co., Jackson, Miss. The small size beads (#4000) were from 1-30 microns in diameter while the large size beads (#325-400) were from 37-44 microns. Surface treatment of beads was accomplished by stirring the beads in carbon tetrachloride at room temperature, with the silane coupling agent, dimethyldichlorosilane (GE SC3002). The main suspending medium was a low molecular weight liquid polybutadiene, Lithene PH, obtained from the Lithium Co. of America. This nonpolar Newtonian

liquid is a mixture of cis and trans polybutadiene which is insoluble in water. The viscosity of the Lithene is 2300 cp, and its density is 0.897 g/cc at 25°C. Two other liquids were tested as main suspending media -- glycerol and Thanol SF-6500 obtained from Jefferson Chemical Co.

Suspensions of glass beads in the different liquids were prepared by introducing the liquid into a flask in which the glass beads were under vacuum. Mixing was then conducted under vacuum for several hours. The well-dispersed suspensions were stored in sealed beakers. The second liquid, water, in most cases, was introduced into the suspension, and the beaker was sealed with a Parafilm cover. The sealed beakers were placed in a sonic vibrating water bath for 2 to 3 days. Cold water flowed continuously through the bath to keep the suspension at low temperature. The formation of agglomerates in the suspensions was observable. After the suspension was taken from the bath, it was mixed further by hand with a spoonula for 30 minutes before making the rheological measurements.

A rotational concentric cylinder viscometer, (Rotovisco, Haake Instruments), was used to measure the rheological behavior of the suspensions at 25°C. Measurements on suspensions started at the highest rotational speeds to minimize the error caused by settling of agglomerates which grew to very large size at low shear rates. Surface tension measurements were made by the ring method. Additional details on the materials and techniques may be found in HPC-74-166 (14).

Results and Discussion

An ideal suspending liquid is one in which the addition of the bridging liquid has little effect on its rheological properties.

Figure 2 indicates that the liquid polybutadiene, Lithene, is ideal,
but glycerol and Thanol are not. Water lowers the viscosity of
glycerol; the amount of lowering is about the same for pure glycerol
and glycerol containing glass beads. Water increases the viscosity
of Thanol. Water has essentially no effect on the viscosity of
Lithene.

The effects of adding water to the suspensions of Lithene and
glass beads are shown in Figures 3 through 7 for representative
experiments. The amount of water is expressed as the ratio of weight
of water to weight of glass beads, W_B/W_S, which is proportional
to the volume of each liquid bridge. In the case of untreated beads,
the water migrates to the surface of the beads, and the resulting
water bridges are responsible for the formation of the agglomerates,
which are visually observable. The suspensions containing water are
all pseudoplastic in their flow behavior. Both the large and small
beads show the same kind of flow curves. In the case of the
dimethyldichlorosilane treated beads, the small beads (#4000) are
agglomerated, but the large beads (#325 + 400) are not. The suspensions
containing large treated beads are essentially Newtonian in behavior
while those containing small treated beads show pseudoplastic flow
behavior. After the small treated beads settle out, the supernatant liquid
is more milky than before the addition of water. Apparently an
emulsion is formed. Therefore, it is speculated that the mechanism of
agglomeration in this case is not all due to liquid bridge formation,
but the mechanism is similar to that observed with treated beads in
glycerol in the absence of water (14). The polar water drops in the
emulsion may be capable of pushing the small beads with a nonpolar

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surface together to form agglomerates because the mutual incompatibility will not allow the emulsion to wet the surface of the treated beads. However, this mechanism for agglomeration fails to operate for the large beads with their reduced surface to volume ratio.

Typical extrapolated Bingham yield stresses and relative plastic viscosities (which are proportional to the straight line sections of the flow curves) are read from the flow curves and are plotted against the amount of water in Figures 8 and 9. It is seen that the yield stress rises rapidly at first to a maximum value around $W_B/W_S = 1.5\%$ and then drops down very slowly. If the packing density inside an agglomerate, ϕ^*, is taken to be 0.55, then the amount of water at which the funicular state is reached can be calculated to be about 6%. The reason why there is a maximum yield value at such a low water content (1.5%) is unknown. This behavior is different from that of wet granular materials which show their highest strength at a much higher water content when the water is in the capillary state. (See Figure 1.)

From equation 15 the Bingham yield stress τ_y can be related to the amount of water W_B/W_S in the suspension as

$$\tau_y = C \left(\frac{W_B}{W_S} \right)^{0.324} \qquad [16]$$

where

$$C = \frac{2.51\sigma \phi^2}{\pi r^2} \left[\frac{0.860\pi\rho_S r^3 (1-\phi^*)}{\rho_B} \right]^{0.324} .$$

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In Figure 8 typical data are fitted to equation 16. The theoretical curve does not predict the maximum in yield stress around $W_B/W_S = 1.5\%$. Also, the constant C evaluated from the material properties used in the suspensions is an order of magnitude lower than the values obtained by fitting the experimental data.

The relative plastic viscosity of the wet to dry suspensions varies irregularly with respect to the amount of water as illustrated in Figure 9. At high enough shear rates for the agglomerates to be broken up, the situation in the suspension can be quite complicated. Since there is a soft water layer around each particle, the applicability of conventional viscosity equations for rigid particles is questionable. Besides, it is possible that the water can be sheared off the particle surfaces and dispersed into the medium as an emulsion.

Because the attractive force caused by liquid bridges is a function of the interfacial tension of the bridging and suspending liquids, it is interesting to see how the reduction of the interfacial tension of the bridge liquid affects the flow behavior of the agglomerated suspensions. A surfactant, Atlas' Tween 20 (polyoxyethylene (20) sorbitan monolaurate), was selected because it had little effect on the viscosity of Lithene. The surface tension of water is reduced from 71.8 dynes/cm to 35.2 dynes/cm when Tween is added. Assuming Antonoff's rule to apply, the Tween should reduce the interfacial tension between water and Lithene from about 34 to 0.5 dynes/cm. The surface tensions being 34.7, 68.7, and 35.2 dynes/cm for Lithene saturated with water, for water saturated with Lithene, and for water containing Tween 20 and Lithene, respectively The suspensions had been agglomerated by adding water prior to the addition of the surfactant. From Figure 10 and Table 1 it is seen that

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the flow curves of suspensions containing Tween 20 differ dramatically from the original agglomerated suspensions. With increasing amounts of Tween, the flow changes from pseudoplastic to Newtonian. Since the surfactant does not alter the flow behavior of Lithene within the concentration range used, the change of flow behavior must be due to the reduction of the attractive force of the liquid bridge as a result of the reduced interfacial tension. The increase in maximum packing fraction on addition of Tween is a good indication of the reduction in the state of agglomeration.

Summary

In this study of the effect of a second immiscible liquid, it is found that water is capable of forming liquid bridges between particles suspended in liquid polybutadiene. The liquid bridges then agglomerate the particles and change the flow behavior from Newtonian to pseudoplastic. The apparent viscosities of agglomerated suspensions can be as high as five times the viscosities of the non-agglomerated suspensions at low rates of shear. The attractive force of liquid bridges is mainly due to the interfacial tension between the two liquids, which can be reduced by surfactants. The flow behavior of suspensions and the attractive force between particles is related for the first time by a theory. However, the theory does not agree well with the experimental data, probably because of several simplifying assumptions made in deriving the theory.

Acknowledgment

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References

1. Haines, W. B., J. Agricultural Sci., <u>15</u>, 529 (1925).

2. Fisher, R. A., J. Agricultural Sci., <u>16</u>, 492 (1926); <u>18</u>, 406 (1928).

3. Carr, J. F., Nature, <u>213</u>, 1158 (1967).

4. Newitt, D. M. and Conway-Jones, J. M., Trans. Inst. Chem. Engrs., <u>36</u>, 422 (1958).

5. Rumpf, H., in "Agglomeration" (W. A. Knepper, Ed.), Interscience, New York, 1962.

6. Pietsch, W., Hoffman, E., and Rumpf, H., Ind. Eng. Chem. Prod. Res. Devel., <u>8</u>, 58 (1969).

7. Kruyt, H. R., and van Selms, F. G., Rec. Trav. Chim., <u>62</u>, 407, 415 (1943).

8. Kao, S. V., D. Sc. Dissertation, Washington University, St. Louis, Mo., 1973.

9. Michaels, A. S., and Bolger, J. C., Ind. Eng. Chem. Fund., <u>1</u>, 153 (1962).

10. Smith, W. O., Foote, P. D., and Busang, P. F., Phys. Rev., <u>34</u>, 1271 (1929).

11. Mason, G., and Clark, W. C., Nature, <u>219</u>, 149 (1968).

12. Clark, W. C., and Mason, G., Nature, <u>216</u>, 826 (1967).

13. Thomas, D. G., J. Colloid Sci., <u>20</u>, 267 (1965).

14. Kao, S. V., Nielsen, L. E., and Hill, C. T., Monsanto/Washington University Association, HPC 74-166 and HPC 74-167, August, 1974.

Table I

Effect of Tween 20 on Properties*

| | Percent of Tween 20 | | | | |
Property	0	0.217	1.02	2.80	4.75
Yield Stress $(Dynes/cm^2)$	2260	300	100	50	0
Apparent Relative Viscosity	1.08	0.942	1.06	1.15	1.24
Maximum Packing Volume Fraction	0.299	0.321	0.346	0.414	0.461

* Volume fraction of beads = 0.30, W_B/W_S = 0.0137

Figures

1. Liquid bridges between spherical particles.

2. Effect of adding small quantities of water to Thanol, Lithene, and glycerol on their viscosity. η_D is the viscosity of the liquids or suspensions containing no water.

3. Flow curves of Lithene containing small untreated glass beads (#4000) with the addition of water. Volume fraction of beads $\phi = 0.20$.

4. Effect of adding water to Lithene containing glass beads (#4000) treated with dimethyldichlorosilane. $\phi = 0.20$.

5. Effect of adding water to Lithene containing large untreated glass beads (#325 + 400). $\phi = 0.20$.

6. Effect of adding water to Lithene containing large glass beads (#325 + 400) treated with dimethyldichlorosilane. $\phi = 0.20$.

7. Effect on the flow curves of adding water to Lithene containing untreated glass beads (#325 + 400). $\phi = 0.30$.

8. The variation of Bingham yield stresses of wet suspensions of Lithene and untreated glass beads (#325 + 400). $\phi = 0.30$. The dotted line is equation 16 with $C = 6500$.

9. The variation of the relative plastic viscosities of the wet to the dry suspensions of Lithene and untreated glass beads (#325 + 400). (a). $\phi = 0.20$. (b). $\phi = 0.30$.

10. Flow curves of suspensions of Lithene and untreated glass beads (#325 + 400) with the addition of water and Tween 20. $\phi = 0.30$.

(a) Liquid Bridge
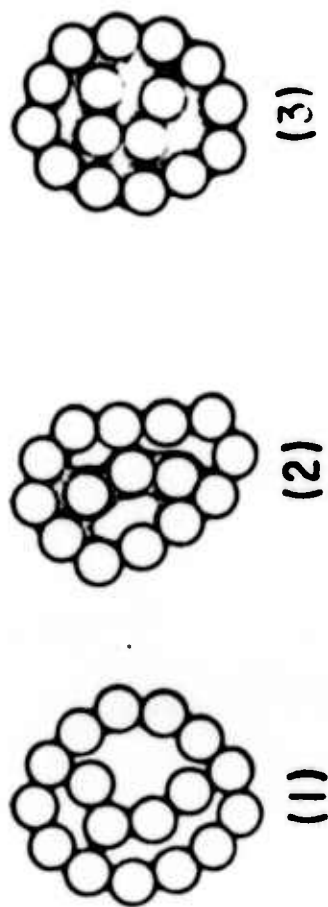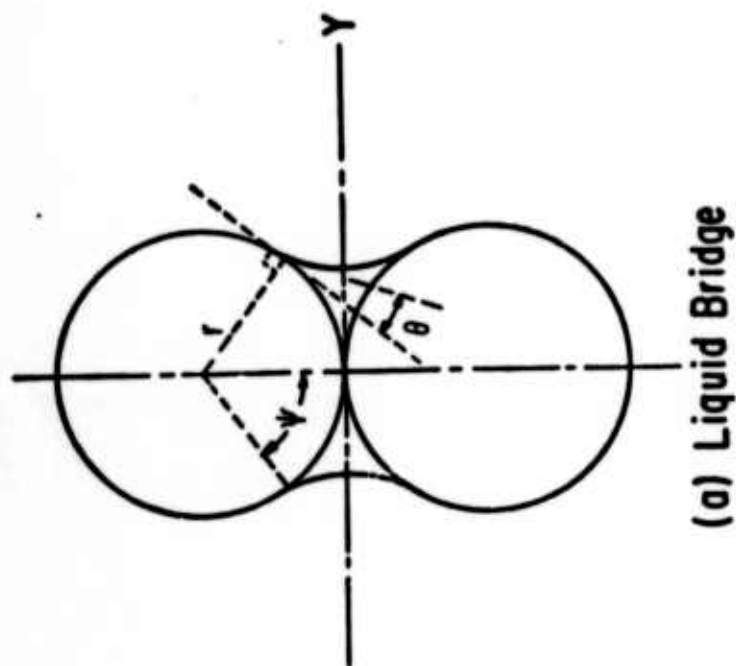
(a) States of Water Content
(1) Pendular State
(2) Funicular State
(3) Capillary State

(1) (2) (3)

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SHEAR STRESS (DYNES/CM²) vs SHEAR RATE (SEC⁻¹)

W_B / W_S (%)

o	0
△	1.30
□	3.24
■	6.48
●	9.91

SHEAR RATE (sec⁻¹)

SHEAR STRESS (dynes/cm²)

WATER(%)

○	0
◐	0.249
□	0.707
●	7.22
◪	10.5

Figure showing SHEAR STRESS (dynes/cm²) versus SHEAR RATE (sec⁻¹) for various WATER (%) content: 0, 0.135, 0.367, 1.69, 5.80.

PERCENT WATER
BASED ON WEIGHT OF GLASS

YIELD STRESS (dynes/cm²)

THEORY

WATER (%)

PERCENT WATER
BASED ON WEIGHT OF GLASS

η_r

η_r

(a)

(b)